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Determination of pesticides in seaweeds by pressurized liquid extraction and programmed temperature vaporization-based large volume injection–gas chromatography–tandem mass spectrometry

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ABSTRACT

A rapid method for the simultaneous identification and quantification of pesticide residues in edible seaweed has been developed. Target analytes were three pyrethroid, a carbamate and two organophosphorus pesticides. The procedure consists of a pressurized liquid extraction (PLE) with integrated clean-up, followed by gas chromatography coupled to tandem mass spectrometry. Five PLE parameters were investigated using a screening design: temperature, static extraction time, number of cycles, percent of flush volume and quantitative composition of the *n*-hexane/ethyl acetate extraction solvent. The effect of the in-cell clean-up with Florisil® and graphitized carbon black adsorbents was investigated using a Doehlert response surface design. Large volumes of sample extracts were injected using a programmed-temperature vaporizer (PTV-LVI) to improve both sensitivity and selectivity of measurements. Quantification was carried by the internal standard method with surrogate deuterated standards. The method showed excellent linearity ($R^2 > 0.999$) and precision (relative standard deviation, RSD $\leq 8\%$) for all compounds, with detection limits ranging from 0.3 pg g^{-1} for chlorpyrifos-ethyl, to 3.0 pg g^{-1} for carbaryl (23.1 pg g^{-1} for deltamethrin). Recoveries in real seaweed samples were within the range 82–108%. The method was satisfactory validated for the analysis of wild and cultivated edible seaweeds. The presence of pyrethroid and organophosphorus pesticides in some of the samples was evidenced.

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1. Introduction

The extensive use of pyrethroid (PYR), organophosphorus (OP) and carbamate (CAR) pesticides may lead to their discharge into surfacewater, groundwater, and soil. Since they are employed as chemotherapeutants in aquaculture, residues of these pollutants and their degradation products can also remain in the marine environment [1]. OP and CAR insecticides interfere with acetylcholine-mediated synaptic transmission in the nervous systems of fish and other aquatic animals via the inhibition of AChE (acetylcholinesterase) enzyme activity [2]. CAR pesticides cause metabolic and behavioural alteration in fish [3]. Most of the PYR compounds are considered endocrine disruptors and affect oestrogens and progesterone hormones [4]. PYR, OP and CAR pesticides are relatively hydrophobic and tend to accumulate on the solid matter of the seawater.

The seaweed industry uses 7.5–8 million metric tonnes of wet seaweeds annually, either from the wild or from cultivated crop. Seaweeds have gained importance as foodstuffs in Western countries and most recently as components of functional foods because of their high dietary fiber, mineral, vitamin, phytochemical content, low energy levels, and high concentrations of certain polyunsaturated fatty acids [5]. The multipurpose uses of seaweed phycocolloids (emulsifiers in dairy products, pharmaceutical industries, food additives commonly used in fast food, etc.) have an immense value. The association of pesticides to the seaweed can produce a bioaccumulative effect along the food chain with the consequent risk for human health [6–9]. Therefore, some aspects of food security and risk assessment studies should be considered before we go ahead for any commercial seaweed exploitation [9].

The extraction of non-polar and semi-polar organic compounds (e.g. PYR, OP and CAR pesticides) from environmental matrices was classically undertaken by Soxhlet, sonication extraction [10,11] or microwave-assisted extraction (MAE) [10,12,13]. The matrix components co-extracted when this procedures are used, are generally removed in successive clean-up steps prior to the chromatographic analysis [14]. Matrix solid-phase dispersion (MSPD) [15] and supercritical fluid extraction (SFE) [16] have been successfully applied for the analysis of trace organic pollutants from biota samples. Both techniques offer the advantage of the simultaneous clean-up of the

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Table 1
Determination of OP, PYR and CAR pesticides in different matrices.

Matrix	Pesticide residues	Extraction procedure	Analytical technique	LOD	Ref.
Water	PYR	SBSE	LD-LVI–GC–MS	0.5 μg L^{-1}	[26]
Water	OP	SPE	GC–ECD/GC–MS/MS	0.1 μg L^{-1}–6.0 ng L^{-1}	[28]
Water	OP	SPE	GC–MIP-AED	17.1–170.3 ng mL^{-1}	[29]
River water	PYR	–	HPLC-PIF	0.02 μg L^{-1}	[41]
Seawater	OP, PYR	SPME	GC–MS/MS	11 pg mL^{-1}	[1]
Ground and seawater	PYR	SPE	LC–ESI-MS	0.5 ng L^{-1}	[31]
Water, vegetables	OP	SPE	HPLC-FD	0.01 ng mL^{-1}	[33]
Vegetables	OP, PYR	PLE	GC–MS	3–8 μg kg^{-1}	[18]
Vegetables	OP	Solvent extraction (DCM)	GC–PFPD	2.0 μg L^{-1}	[35]
Vegetables	PYR	Solvent extraction (DCM)	LC–ESI-MS	3.0 ng g^{-1}	[39]
Vegetables	PYR	Solvent extraction (DCM)	HPLC-CL	0.04 μg mL^{-1}	[40]
Fruits, vegetables	OP, PYR, CAR	Solvent extraction (acetone) + RP-SPE	PTV-LVI–GC–MS/MS	–	[25]
Fruits, vegetables	OP, PYR	SFE	GC–ECD	0.01 mg kg^{-1}	[38]
Fruits, vegetables	CAR	PHWE	GC–FE	1 μg mL^{-1}	[42]
Avocado	OP, PYR	PLE-GPC	LP-GC–MS/MS	0.01–2.50 μg kg^{-1}	[43]
Juice	OP	SDME	GC–FPD	1.0 μg L^{-1}	[30]
Meat	OP	GPC	GC–MS/MS	10 ng mL^{-1}	[36]
Urine, plasma	CAR	SPE	GC–MS	34 μg mL^{-1}	[8]
Urine	OP, PYR	SPE	HPLC-TIS–MS/MS/HPLC-APCI-MS/MS	0.5 ng mL^{-1}	[34]
Urine	OP	SPE	GC–MS/MS	0.1 ng mL^{-1}	[37]
Soil	PYR	FTE	LVI-HPLC (UV)	0.3 mg kg^{-1}	[27]
Soil	OP	PLE	GC–MS	4.6 μg kg^{-1}	[44]
Sediment	OP, PYR	UAE	GC–ECD	0.6 μg kg^{-1}	[32]
Compost	OP, PYR, CAR	PLE + LLE	GC–MS	0.02–0.03 μg g^{-1}	[22]

extracts. Table 1 summarizes analytical procedures that have been used to determine PYR, OP and CAR pesticides in different sample matrices.

Pressurized liquid extraction (PLE) has been successfully applied for the extraction of persistent organic pollutants from different matrices as soil, compost, vegetables or fish with off-line clean-up or integrated clean-up [17–24]. Integration of the PLE and cleanup operations has also been achieved by loading a matrix retainer (Florisil®, H_2SO_4/silica, alumina or carbon) at the bottom of the PLE extraction cell [19,20,23]. In this work, a one-step extraction and cleanup PLE procedure for PYR, OP and CAR pesticides is evaluated using a mixture of Florisil® and graphitized carbon black (GCB). The main advantages are a substantial reduction of the extraction time (2 min), the solvent volume and the small amount of sample and adsorbents required (11 mL cells).

Tandem mass spectrometry (MS/MS) using a low-resolution ion-trap mass spectrometer is a very selective technique which is widely employed for pollutant analysis in food. There are two common ways for increasing sensitivity of chromatography determinations: to increase of the sample size and to inject large volumes of sample into the gas chromatography column. In both cases an extensive extract cleanup is required. Large volume injection with a programmed-temperature vaporizer (PTV-LVI) combined with GC coupled to MS or MS/MS has been previously employed for the determination of pesticide residues in fruits, vegetables [25] and water [26] or flame retardants in urban dust [45]. Also, it has been used HPLC methodologies to determine PYR in soil [27]. In this way the sensitivity was considerably increased, compared to the use of conventional split/splitless injectors. So, PTV-LVI coupled to GC–MS/MS appears to be a good alternative to more sensitive high resolution mass spectrometry (HRMS) equipments, offering a positive balance between sensitivity, versatility, and cost. To the best of our knowledge there are no reports in the literature concerning the application of PLE–PTV-LVI–GC–MS/MS for the multiresidue extraction of OP, PYR and CAR pesticides in seaweed samples.

The aim of this paper is to describe a selective PLE method with in-cell clean-up for the extraction of aquaculture pesticides from edible seaweed and their subsequent analysis by GC–MS/MS. The target analytes were three pyrethroid (permethrin, α-cypermethrin and deltamethrin), a carbamate (carbaryl) and two organophosphorus pesticides (chlorpyrifos-ethyl and chlorpyrifos-methyl). Extraction conditions were optimized by means of experimental designs involving desirability functions. Moreover, a practical and efficient analysis method for OP, PYR and CAR pesticides have been developed based on GC–MS/MS operating in electron impact (EI) mode with a programmable temperature inlet and large volume injection. The developed method was also compared with other methodologies based on traditional GC–MS/MS and GC–μECD and its performance was characterized in terms of accuracy, precision, linearity and LODs. Finally, the method was applied to the analysis of real seaweed samples.

2. Experimental

2.1. Standards and materials

Pestanal quality analytical standards of α-cypermethrin (cyclopropanecarboxylic acid, 3-(2,2-dichloroethenyl)-2,2-dimethyl-(R)-cyano(3-phenoxyphenyl)methylester) (99.8%), chropiryfos-ethyl (phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester) (99.2%), chropiryfos-methyl (phosphorothioic acid, O,O-dimethyl O-(3,5,6-trichloro-2-pyridinyl) ester) (99.7%), carbaryl (1-naphthyl-N-methylcarbamate) (99.8%) and permethrin (cyclopropanecarboxylic acid, 3-(2,2-dichloroethenyl)-2,2-dimethyl-, (3-phenoxyphenyl)methyl ester) (99.3%) were from Riedel-de Haën (Seelze, Germany). Deltamethrin (cyclopropanecarboxylic acid, 3-(2,2-dibromoethenyl)-2,2-dimethyl-(S)-cyano (3-phenoxyphenyl)methyl ester) (99.0%) was from Chem Service Inc. (West Chester, PA, USA). (Diethyl-D_{10})-chropiryfos (100 μg mL^{-1} in nonane) and (phenoxi-$^{13}C_6$)-*cis*-permethrin (50 μg mL^{-1} in nonane) were from Cambridge Isotope Laboratories (Cambridge, UK). Ethyl acetate (Chromanorm), acetone (Pestinorm), *n*-hexane (Pestinorm) and dichloromethane (Pestinorm) were from VWR-Prolabo (Mollet del Vallés, Barcelona, Spain). Methanol (gradient HPLC grade) was from Merk (Darmstadt, Germany).

Stock solutions of each individual pesticide at 5000 μg mL^{-1} and of the six studied pesticides together were prepared in acetone and were stored at −18 °C.

Sodium sulphate anhydrous was from Panreac (Barcelona, Spain). Florisil® (60–100 mesh), sea sand (50–70 mesh) and aluminium oxide activated neutral (150 mesh) were from Aldrich

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